STUDY OF TETRAETHYLAMMOMIUM HYDROXIDE AS AN ALTERNATIVE FOR TMAH DEVELOPER IN ELECTRON BEAM AND PHOTOLITHOGRAPHY

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Tetramethylammonium hydroxide (TMAH) is a strong base widely used in the semiconductor industry as a metal-ion-free alternative to potassium hydroxide and sodium hydroxide for wet etching, photoresist development, and photoresist cleaning/stripping. The lack of metal ions removes risks to CMOS devices from the highly mobile sodium and potassium ions, but TMAH is dermally toxic [1] for concentrations above 1% by weight [2] with no known antidote. Toxicity scales with body surface area coverage and concentration [3], with concentrated 25% TMAH being used for wet etching and high-contrast development of hydrogen silsesquioxane (HSQ), and 2.38% being commonly used for DNQ/Novolac photoresist development. Considering the dermal toxicity hazard of TMAH, especially in labs specializing in research, development, and teaching, where TMAH is typically used in open dishes, it would be desirable to find a less toxic metal-ion-free developer for photon and electron beam lithography (EBL).We compared developer based on the less toxic tetraethylammonium hydroxide (TEAH) to standard TMAH for typical positive and negative photoresists for broadband contact lithography and direct write laser lithography. Additionally, we tested both low and high concentration TMAH and TEAH for HSQ (H-SiQ from Dischem) EBL. We purchased 0.26 N (wt. 4%) TEAH in water (Novosafe Developer SE-44-26) and concentrated 35% TEAH in water (Novosafe SE-44) from Transene Corporation. TMAH based developers were either 0.26 N (wt. 2.38%) TMAH (CD-26) in water or concentrated 25% TMAH.

For the positive resist SPR955, we observed an increased (~2.5x) dose is required to develop the same thickness of resist for the same amount of time with SE-44-26 versus CD-26. Figure 1 shows the optical microscope and SEM images of SPR955 developed using SE-44-26 and CD-26 of nominally 2um lines. For the negative resist AZnLOF2020 exposed via contact lithography, we observed an interesting result where the side profile of the feature changes from positive slope to negative slope (undercut) with increased developing time for SE-44-26 developer. Figure 2 shows the cross-sectional SEM image of nLoF2020 resist after 2.5mins, 3.5mins, 5mins and 10mins of development.

We also present a comparison of EBL exposed HSQ (EBPG5000) developed in SE-44-26, 35% TEAH (SE-44), CD-26 and 25% TMAH. We observed that a 100 nm pillar array was resolved using 35% SE-44 at room temperature and required lesser dose than concentrated TMAH as shown in Fig.3. However, for low concentration SE44 and CD-26, the resist did not completely clear with some residue in between features.

We are still investigating patterns processed using a direct writing photolithography tool (Heidelberg MLA150) and will present the results during the talk.

[1]:https://doi.org/10.3109/15563651003627777
[2]:https://sesha.org/abstract/tetramethylammonium-hydroxide-tmah-toxicity-and-methods-to-reduce-risk-in-the-workplace/
[3]:https://doi.org/10.1016/j.burns.2012.02.027
[4]: https://www.jksem.org/upload/pdf/jksem-33-3-322.pdf

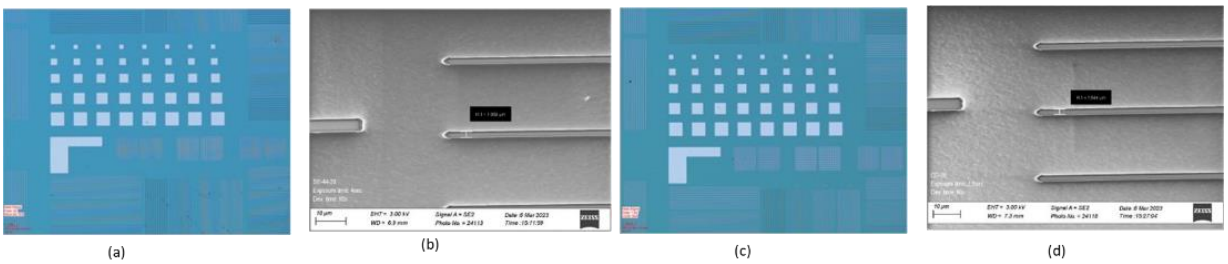
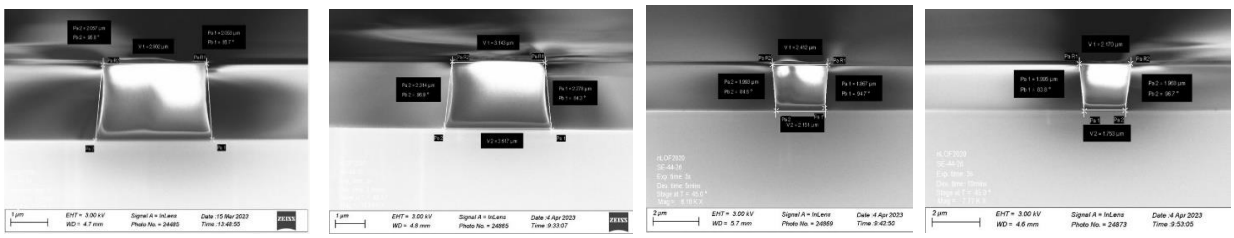


Figure 1: Optical microscope image and SEM image of nominally 2um lines in (a, b) SPR955 dosed for 4s and developed using SE44 for 90s (c, d) SPR955 dosed for 1.5s and developed using CD-26 for 90s.



(a) (b) (c) (d)

Figure 2: Cross-sectional SEM image of nLoF2020 resist exposed for 3s on contact aligner and developed for (a) 2.5mins (b) 3.5mins (c) 5mins and (d)10mins.

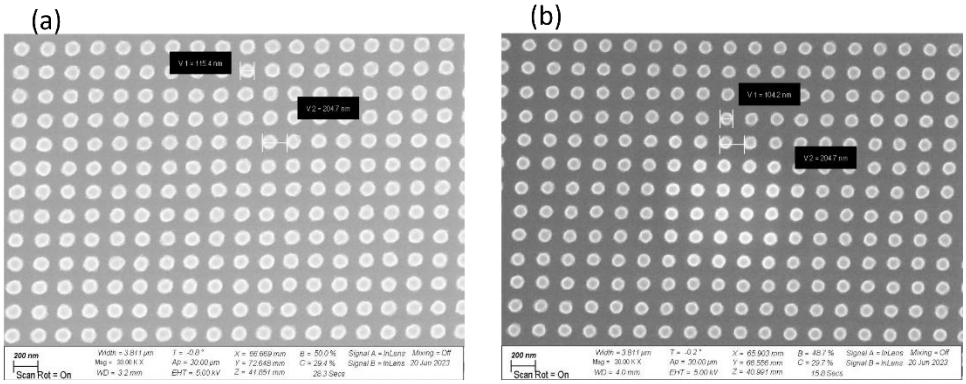


Figure 3: SEM image of nominally 100nm HSQ resist pillars using e-beam lithography (a) Dose of 1000uC/cm^2 developed using 35% SE-44 (b) Dose of 2000uC/cm^2 developed using 25% TMAH at room temperature.